

(19) World Intellectual Property Organization
International Bureau(43) International Publication Date
29 March 2001 (29.03.2001)

PCT

(10) International Publication Number
WO 01/21697 A1

- (51) International Patent Classification: C08K 5/13, C08G 59/62, 59/42, C08K 5/00, C08G 59/68 // (C08K 5/00, 5:19, 5:375, 5:50)
- (21) International Application Number: PCT/EP00/09187
- (22) International Filing Date: 15 September 2000 (15.09.2000)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data: 301479/99 17 September 1999 (17.09.1999) JP
- (71) Applicant (for all designated States except US): SHELL INTERNATIONAL RESEARCH MAATSCHAPPIJ B.V. (NL/NL); Carel van Bylandtlaan 30, NL-2596 HR The Hague (NL).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): HAYAKAWA, Atsuhito [JP/JP]; I Banchi Shiohama-cho, Yokkaichi-city, Mie -pref 510 (JP). MURATA, Yasuyuki [JP/JP]; I Banchi Shiohama-cho, Yokkaichi-city, Mie -pref 510 (JP).
- (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
- Published:
- With international search report.
 - Before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments.
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



WO 01/21697 A1

(54) Title: EPOXY RESIN COMPOSITION AND RESIN ENCAPSULATION TYPE SEMICONDUCTOR DEVICE

(57) Abstract: The present invention provides an epoxy resin composition that gives a cured product having rapid curability, excellent fluidity, low moisture absorption and adhesiveness, and a resin encapsulation-type semiconductor device having excellent solder crack resistance, encapsulated with this composition. An epoxy resin composition comprising a blend of (a) an epoxy resin, (b) a compound having two or more phenolic hydroxyl groups on the average in one molecule and (c) a cationic polymerization catalyst for epoxy resin, as the essential components, and a semiconductor device encapsulated with this composition.

EPOXY RESIN COMPOSITION AND RESIN ENCAPSULATION
TYPE SEMICONDUCTOR DEVICE

5 The present invention relates to an epoxy resin composition which has excellent, rapid curability and fluidity and gives a cured product having excellent low moisture absorption, adhesiveness, etc., and to a resin encapsulation type semiconductor device having excellent solder crack resistance, in which a semiconductor element is encapsulated with the composition.

10 Epoxy resin compositions are widely used in the fields of adhesion, casting, encapsulation, lamination, molding, coating and the like, because they have excellent adhesion, curing property and are easy to handle. In addition, there are various kinds of epoxy resin compositions and their molding methods. Since the
15 moldability and curing property thereof markedly vary depending on the selection therefrom, epoxy resin compositions are appropriately employed according to their use fields or to their purposes.

In recent years, as the use conditions of polymeric materials become severer, various strict characteristics
20 are required to the polymeric materials. As a result, not every type of epoxy resins generally employed, can sufficiently satisfy the required characteristics.

For example, compositions having blended therein an epoxy resin and a phenolic resin hardener in an almost
25 equivalent amount and a catalyst for the reaction of epoxy groups and phenolic groups, are widely used for semiconductor encapsulation. However, the required performances become stricter even in this field.

30 That is, high integration of semiconductor devices proceeds, with the result that the enlargement of the

semiconductor elements per space unit becomes remarkable, as well as that their packages are miniaturized and thinned. Further, the mounting technology of the semiconductor devices transfers to a surface mounting.

5 In the surface mounting, a semiconductor device is directly dipped in a solder bath and therefore exposed to high temperature. Accordingly, moisture absorbed therein rapidly expands, and interface separations between resin, inner semiconductor element, etc. occur. As a result, this causes cracks in an encapsulant. For this reason, an epoxy resin composition for an encapsulant with good solder crack resistance is required to have high heat resistance, that is, high glass transition temperature, low moisture absorption, and high adhesiveness.

10 In addition, with employment of small-sized and thin-sized packages, high fluidity is also required to an epoxy resin composition for encapsulant.

The epoxy resin compositions mainly used at present as stated above have not been considered to be sufficient in such points of rapid curability, fluidity, or low moisture absorption.

Japanese Patent Application Laid-open
Nos. Hei 3-115427 and Hei 8-213417 disclose compositions having blended therein an epoxy resin and a specific
25 onium salt compound as a cationic polymerization catalyst. However, cured products obtained from those compositions are superior in rapid curability and low moisture, but inferior in adhesiveness.

Therefore the present invention has an object to
30 provide an epoxy resin composition which has excellent rapid curability and fluidity, and gives a cured product having excellent low moisture absorption and adhesiveness, and to provide a resin encapsulation type semiconductor device having excellent solder crack

resistance, in which a semiconductor element is encapsulated with the composition.

5 As a result of various investigations to solve the above-mentioned problems, the inventors of the present invention have achieved the object by using a composition having a phenolic compound added thereto in a system using a cationic polymerization catalyst as a hardener.

Accordingly, the epoxy resin composition of the present invention relates to:

10 An epoxy resin composition comprising a blend of:

(a) an epoxy resin;

(b) a compound having two or more phenolic hydroxyl groups on the average in one molecule; and

15 (c) a cationic polymerization catalyst for epoxy resin, as essential components.

In particular the invention relates to an epoxy resin composition as described hereinbefore, wherein the epoxy resin (a) is an epoxy resin that can be handled as a solid at room temperature, and has a melt viscosity at 20 150 °C of 2.0 poise or less.

Preferably, the epoxy resin is either an amorphous epoxy resin having a softening point of 50 °C or higher or the epoxy resin is a crystalline epoxy resin having a melting point of 40 °C or higher.

25 In the hereinbefore defined epoxy resin composition preferably the compound (b) having two or more phenolic hydroxyl groups on the average in one molecule is blended in an amount so that the phenolic hydroxyl group is 0.05-0.8 mole per one mole of epoxy group in the epoxy resin.

30 More preferably the cationic polymerization catalyst (c) for epoxy resin is at least one selected from ammonium salts, sulfonium salts, phosphonium salts and pyridium salts of hexafluorophosphoric acid or hexafluoroantimonic acid.

According to a more preferred embodiment of the epoxy resin composition of the present invention, the amount of the cationic polymerization catalyst is 0.01-15 parts by weight per 100 parts by weight of the epoxy resin as the component (a).

According to more preferred embodiments, in addition to components (a), (b) and (c), fused and/or crystalline silica powder fillers are blended as an inorganic filler (d) in an amount of 40-95% by weight based on the weight of the entire composition.

It will be appreciated that the invention is also relating to a resin encapsulation type semiconductor device, wherein a semiconductor element is encapsulated with a cured product of the epoxy resin composition as described hereinbefore.

In the conventional epoxy resin compositions for semiconductor encapsulation, a method have been employed in which a phenolic resin hardener is blended with an epoxy resin in almost equivalent amount, and hardening the composition with a catalyst for the reaction of epoxy groups and phenolic hydroxyl groups. However, in this method, rapid curing property is inferior. In addition, a phenolic resin hardener having high melt-viscosity is blended in large amount, so that fluidity thereof upon molding is also inferior.

The present invention employs a curing method in which cationic polymerization is used which is excellent in rapid curing. In addition, adhesiveness that is inferior in this method is remarkably improved by adding a phenolic resin hardener in a small amount to such an extent that fluidity is not impaired.

The epoxy resin (a) used in the epoxy resin composition of the present invention is not particularly limited, and a variety of epoxy resins can be used.

Examples of the epoxy resin include epoxy resins obtained from various phenol type compounds such as polyhydric phenolic resins obtained by condensation reaction of various phenols (e.g., bisphenol A, bisphenol F, bisphenol AD, biphenol, tetramethyl biphenol, 5 tetramethyl bisphenol F, hydroquinone, methyl hydroquinone, dibutyl hydroquinone, resorcin, methyl resorcin, dihydroxydiphenyl ether, dihydroxystilbene derivatives, dihydroxynaphthalene, phenol novolak resin, 10 cresol novolak resin, naphthol novolak resin, bisphenol A novolak resin, phenol aralkyl resin, terphenenol resin, dicyclopentadienephenolic resin, brominated bisphenol A, and brominated phenol novolak resin), with various aldehydes (e.g., benzaldehyde, hydroxybenzaldehyde, 15 crotonaldehyde, and glyoxal), and an epihalohydrin; epoxy resins produced from various amines (e.g., diaminodiphenyl methane, aminophenol and xylenediamine), and an epihalohydrin; epoxy resins produced from various carboxylic acids (e.g., methylhexahydroxyphthalic acid 20 and dimer acid), and an epihalohydrin; hydrogenated epoxy resins such as hydrogenated bisphenol A type epoxy resin and hydrogenated bisphenol F epoxy resin; and alicyclic epoxy resins such as 1,2-epoxyethyl-3,4-epoxycyclohexane, 3,4-epoxycyclohexylcarboxylic acid-3,4-epoxycyclohexyl- 25 methyl and bis(3,4-epoxy-6-methylcyclohexylmethyl) adipate.

In the case where the epoxy resin composition of the present invention is used for encapsulating a semiconductor by a low pressure transfer molding method, 30 among the above-mentioned various epoxy resins, ones that can be handled as a solid at room temperature may be used as the epoxy resin (a) of the present invention.

In order to handle the epoxy resin as a solid at room temperature, in the case where the epoxy resin is 35 amorphous, it is necessary to have a softening point of

50 °C or higher, preferably 55 °C or higher. In the case that the epoxy resin is crystalline, it is necessary to have a melting point of 40 °C or higher, preferably 45 °C or higher.

5 Further, it is preferable that the epoxy resin (a) used in this application has low melt viscosity in order to make the fluidity good. The melt viscosity thereof at 150 °C is preferably 2.0 poise or less, more preferably, 1.0 poise or less.

10 Those epoxy resins may be used as one kind alone or as a mixture of two kinds or more. In the case of using two kinds or more of the epoxy resins, each epoxy resin needs not to satisfy such conditions of being solid at room temperature and having low melt viscosity. If the
15 mixture of the epoxy resins satisfy the above-mentioned conditions, the epoxy resins can be used for encapsulating the semiconductors by the low-pressure transfer molding method.

Of various epoxy resins, in view of being easy to
20 obtain, their curing properties, etc., at least one kind of epoxy resin selected from bisphenol A type epoxy resin, bisphenol F type epoxy resin, biphenol type epoxy resin, tetramethylbiphenol type epoxy resin, phenol novolak type epoxy resin, cresol novolak type epoxy
25 resin, bisphenol A type novolak epoxy resin, terpene phenol type epoxy resin and dicyclopentadiene phenol type epoxy resin is preferable.

The compound (b) having two or more phenolic hydroxyl groups on the average in one molecule is blended as an
30 essential component into the epoxy resin composition of the present invention.

Examples of the compound having two or more phenolic hydroxyl groups on the average in one molecule include various polyhydric phenols (e.g., bisphenol A, bisphenol
35 F, bisphenol AD, hydroquinone, resorcin, methylresorcin,

biphenol, tetramethylbiphenol, dihydroxynaphthalene, dihydroxydiphenyl ether, allylated bisphenol A, allylated bisphenol F, phenol novolak resin, cresol novolak resin, bisphenol A novolak resin, phenol aralkyl resin, terpene phenol resin, dicyclopentadiene phenolic resin, naphthol novolak resin, brominated bisphenol A and brominated phenol novolak resin) and polyhydric phenolic resins obtained by condensation reaction of various phenols and various aldehydes (e.g., benzaldehyde, hydroxybenzaldehyde, crotonaldehyde and glyoxal).

The compound having two or more phenolic hydroxyl groups on the average in one molecule is used in such a proportion that the amount of phenolic hydroxyl groups in the phenolic hydroxyl group-containing compound is preferably 0.05-0.8 mol, more preferably 0.1-0.6 mol, most preferably 0.1-0.5 mol, per one mole of the epoxy groups in the epoxy resin. If the proportion of the compound having two or more phenolic hydroxyl groups on the average in one molecule to be used is too large, rapid curability, fluidity and low moisture absorption are not sufficiently exhibited. If the proportion of the compound having two or more phenolic hydroxyl groups on the average in one molecule to be used is too small, adhesiveness is not sufficient.

The cationic polymerization catalyst (c) for epoxy resin is blended into the epoxy resin composition of the present invention. This catalyst is a substance that initiates cationic ring-opening polymerization of epoxy groups, and heat cationic polymerization initiators that generate cation species or Lewis acid by heat can be used.

Examples of the cationic polymerization initiator that can be used include triflic acid salts, boron trifluoride ether complex compounds, metal fluoroboron complex salts, bis(perfluoroalkylsulfonyl)methane metal

salts, aryl diazonium compounds, aromatic onium salts, dicarboxylates of Groups IIIa-Va elements, thiopyrylium salts, VIb elements in the form of MF_6^- (wherein M is selected from phosphorus, antimony and arsenic),
5 arylsulfonium complex salts, aromatic iodonium complex salts, aromatic sulfonium complex salts, bis[4-(diphenylsulfonio)phenyl]sulfide-bis-hexafluoro metal salts (for example, phosphorus salts, arsenides, antimonates or the like), aryl sulfonium complex salts and aromatic
10 sulfonium or iodonium salts of halogen-containing complex ions.

Of those cationic polymerization initiators, aromatic onium salts are preferable from the view points of being excellent in handling property and in balance between
15 latent property and curability, and ammonium salts, sulfonium salts, phosphonium salts or pyridium salts of hexafluoroantimonic acid or hexafluorophosphoric acid are more preferable.

The amount of the cationic polymerization catalyst to be used is preferably 0.01-15 parts by weight, more preferably 0.1-10 parts by weight, per 100 parts by weight of the epoxy resin as component (a).
20

If the amount of the catalyst falls outside the herein before-mentioned range, the balance between heat
25 resistance and moisture resistance in the cured epoxy resin product becomes poor, which is undesirable.

In the case of using the epoxy resin composition of the present invention for encapsulating the
semiconductors, it is preferable to blend an inorganic
30 filler (d) thereinto. Examples of the inorganic filler include fused silica, crystalline silica, glass powder, alumina and calcium carbonate. The shape thereof is crushed form or spherical form. Various inorganic fillers are used alone or as mixtures of two kinds or

more, and of those, fused silica or crystalline silica is preferable. The amount of the inorganic filler to be used is 40-95% by weight, preferably 80-93% by weight, more preferably 83-93% by weight, of the entire composition in the case of a solid encapsulant used in the low-pressure transfer molding method. In the case of a liquid encapsulant used in potting or underfill, the amount is preferably 40-80% by weight, particularly preferably 50-75% by weight, of the entire composition.

If the amount of the inorganic filler (d) used is too small, the moisture absorption is not low enough, resulting in poor solder crack resistance. If the amount of the inorganic filler (d) used is too large, fluidity in molding is impaired.

Epoxy resin hardeners other than the phenol compounds, cure accelerators, flame retardants, flame retardant aids, coupling agents, ion capturing agents, plasticizers, pigments, solvents, release agents, reinforcing fibers or the like can appropriately be blended as required into the epoxy resin composition of the present invention.

Examples of the epoxy resin hardeners other than the phenol compounds include acid anhydrides such as methyl-tetrahydrophthalic anhydride, hexahydrophthalic anhydride, pyromellitic anhydride or methyl nadic acid; and amines such as diethylene triamine, isophorone diamine, diaminodiphenyl methane, diaminodiphenyl sulfone or dicyandiamide.

The proportion of those epoxy resin hardeners to be used, other than the phenol compounds, is in such an amount that the sum of phenolic hydroxyl groups in the phenolic hydroxyl group-containing compound (b) and groups that react with epoxy groups in the epoxy resin hardeners other than phenol compounds, is 0.8 mol or less per one mole of epoxy groups in the epoxy resin. If the

proportion of the epoxy resin hardener to be used, other than phenol compound, is too large, the effect of the present invention is not sufficiently exhibited.

5 The cure accelerator is a compound that accelerates the reaction between epoxy groups in the epoxy resin and active groups in the hardener. Examples thereof include phosphine compounds such as tributylphosphine or tri-phenylphosphine; phosphonium salts such as tetraphenyl-phosphonium tetraphenyl borate; imidazoles such as 2-10 methyl imidazole or 2-phenylimidazole, 2-ethyl-4-methyl imidazole; amines such as 2,4,6-tris(dimethylamino-methyl)phenol or benzyldimethyl amine; ammonium salts such as triethylammonium tetraphenyl borate; diazabicyclo compounds such as 1,5-diazabicyclo(5,4,0)-7-undecene, and 15 tetraphenyl borates, phenol salts, phenol novolak salts, 2-ethylhexanoic acid salts or the like of those diazobicyclo compounds.

 Further, antimony trioxide, phosphoric acid, molybdenum oxide or the like can appropriately be blended 20 thereinto as the flame retardant aid.

 The resin encapsulation-type semiconductor device according to the present invention is a semiconductor device in which semiconductor elements such as an 25 integrated circuit, very large scale integrated circuit, transistors, thyristor, diode or the like are encapsulated with a cured product of the epoxy resin composition according to the present invention. Kinds of the semiconductor elements, their encapsulating method, the shapes of encapsulation and the like are not 30 particularly limited.

 The encapsulating methods include the low pressure transfer molding method and injection molding method using a solid epoxy resin composition at room temperature, potting method, screen printing method, and

underfill method using a liquid epoxy resin composition at room temperature, and the like.

The curing conditions after molding depend upon the kinds of the respective components of the epoxy resin composition, and the amounts blended thereof, but generally comprise a temperature of from 150 to 220 °C during a period of from 30 seconds to 10 hours.

The epoxy resin composition of the present invention is excellent in rapid curability and fluidity, and gives a cured product having excellent low moisture absorption, adhesiveness and the like, and therefore can advantageously be used in the field of semiconductor encapsulation or the like.

The resin encapsulation-type semiconductor device of the present invention has excellent solder crack resistance, and therefore can advantageously be used in surface mounting method.

The epoxy resin composition and an epoxy encapsulation-type semiconductor device according to the present invention will be hereinafter described in detail with reference to examples and comparative examples, however without restricting the scope to these embodiments.

EXAMPLES 1-3 AND COMPARATIVE EXAMPLE 1

As shown in Table 1, each epoxy resin composition was formulated by using bisphenol A type epoxy resin or bisphenol F type epoxy resin as the epoxy resin (a), bisphenol F as the compound (b) having two or more phenolic hydroxyl groups on the average in one molecule, and dimethylphenyl(4-methoxybenzyl)ammonium hexafluoroantimonate or methyl(4-methoxyphenyl)(1-naphthylmethyl)-sulfonium hexafluoroantimonate as the cationic polymerization catalyst (c) for epoxy resin, and mixing them to prepare a uniform solution. Viscosity at 25 °C

of each composition was measured. Further, gel time at 150 °C was measured. The results are shown in Table 1.

Next, the above composition was defoamed, poured into a mold, and then cured in an oven at 90 °C for 2 hours and further at 150 °C for 2 hours to obtain a colorless, transparent cured product. Further, a test piece for shear adhesion measurement was prepared and cured in the same manner. Measurement values of water absorption, glass transition temperature and shear adhesive strength of this cured product are shown in Table 1. Each composition of Examples 1-3 did not have great deterioration in rapid curability (that is, short gel time), fluidity (that is, low viscosity) and low water absorption as compared with the composition of Comparative Example 1, and high adhesiveness was greatly excellent.

EXAMPLES 4-6 AND COMPARATIVE EXAMPLES 2 AND 3

Each epoxy resin composition was formulated by using cresol novolak type epoxy resin or tetramethylbiphenol type epoxy resin as the epoxy resin (a), brominated bisphenol A type epoxy resin as the flame retardant, phenol novolak resin or phenol aralkyl resin as the compound (b) having two or more phenolic hydroxyl groups on the average in one molecule, methyl(4-methoxyphenyl)-(1-naphthylmethyl)sulfonium hexafluoroantimonate, methyl(4-hydroxyphenyl)benzylsulfonium hexafluoroantimonate or triphenyl(4-chlorobenzyl)phosphonium hexafluoroantimonate as the cationic polymerization catalyst (c) for epoxy resin, spherical fused silica powder as the inorganic filler (d) in an amount of 85% by weight of the entire composition, antimony trioxide as the flame retardant aid, epoxysilane as the filler surface treating agent, and carnauba wax as a release agent, and also using triphenylphosphine as the cure accelerator in Comparative Example 2, as shown in Table 2.

Next, each blend was melt mixed at a temperature of 70-130 °C for 5 minutes using mixing rolls. Each molten mixture obtained was taken out in the form of sheet, and the sheet was crushed to obtain each molding material.

5 Gel time at 180 °C of each molding material was measured.

Each molding material was molded with a low pressure transfer molding machine at a mold temperature of 180 °C for a molding time of 90 seconds to obtain each test piece and 160 pin TQFP type resin encapsulation type semiconductor device, and these are post-cured at 180 °C for 5 hours. Further, spiral flow of each molding material was measured.

10 The results of gel time and spiral flow of each molding material, glass transition temperature and moisture absorption of each test piece after post-cure, and solder crack resistance of each resin encapsulation type semiconductor device are shown in Table 2. Each composition of Examples 4-6 were greatly excellent in balance of rapid curability (that is, short gel time), fluidity (that is, high spiral flow), low moisture absorption and solder crack resistance, as compared with the compositions of Comparative Examples 2 or 3.

Table 1

| | Example | | | Comparative Example 1 |
|---|---------|------|------|--------------------------|
| | 1 | 2 | 3 | |
| Epoxy resin composition formulation (parts by weight) | | | | |
| (a) Epoxy resin | A*1 | A*1 | B*2 | A*1 |
| Blending amount | 100 | 100 | 100 | 100 |
| (b) Phenol compound | C*3 | C*3 | C*3 | - |
| Blending amount | 10 | 20 | 15 | 0.0 |
| Hydroxyl group/epoxy group equivalent Ratio | 0.18 | 0.35 | 0.24 | 0.0 |
| (c) Cationic polymerization catalyst | D*4 | E*5 | E*5 | E*5 |
| Blending amount | 1.0 | 1.5 | 1.0 | 1.5 |
| Viscosity (PS at 25 °C) | 161 | 180 | 50 | 136 |
| Gel time (second at 150 °C) | 47 | 37 | 53 | 35 |
| Curing properties | | | | |
| Water absorption (%) *6 | 0.28 | 0.30 | 0.31 | 0.28 |
| Glass transition temperature (°C) *7 | 131 | 128 | 125 | 134 |
| Shear adhesive strength (kg/cm ²) | 160 | 210 | 190 | 18 |

(Notes)

*1: A; Bisphenol A type epoxy resin (trade name of Yuka shell Epoxy K.K., Epikote 828, epoxy equivalent: 186)

*2: B; Bisphenol F type epoxy resin (trade name of Yuka shell Epoxy K.K., Epikote 807, epoxy equivalent: 171)

*3: C; Bisphenol F (a product of Mitsui Chemical Inc.)

*4: D; Dimethylphenyl(4-methoxybenzyl)ammonium hexafluoroantimonate

*5: E; Methyl(4-methoxyphenyl)(1-naphthylmethyl)sulfonium hexafluoroantimonate

*6: Boiling water absorption, 100 °C, 1 hour

*7: Obtained by TMA from transition point on the thermal expansion curve

5

Table 2

| | Example | | | Comparative Example | |
|---|---------|------|------|---------------------|------|
| | 4 | 5 | 6 | 2 | 3 |
| Epoxy resin composition formulation (parts by weight) | | | | | |
| (a) Epoxy resin | | | | | |
| Epoxy resin I | F*1 | F*1 | G*2 | F*1 | F*1 |
| Blending amount | 90 | 70 | 100 | 90 | 90 |
| Epoxy resin II | - | G*2 | - | - | - |
| Blending amount | - | 20 | - | - | - |
| Epoxy resin III | H*3 | H*3 | - | H*3 | H*3 |
| Blending amount | 10 | 10 | - | 10 | 10 |
| Epoxy resin melt viscosity *4 | 2.9 | 1.6 | 0.2 | 2.9 | 2.9 |
| (b) Phenol compound | I*5 | I*5 | J*6 | I*5 | - |
| Blending amount | 7 | 14 | 18 | 47 | 0.0 |
| Hydroxyl group/epoxy group equivalent ratio *7 | 0.15 | 0.30 | 0.20 | 1.0 | 0.0 |
| (c) Cationic polymerization catalyst | K*8 | L*9 | M*10 | - | K*8 |
| Blending amount | 1.0 | 1.0 | 1.5 | 0.0 | 1.0 |
| (d) Inorganic filler *11 | 680 | 722 | 744 | 905 | 640 |
| Triphenylphosphine | 0.0 | 0.0 | 0.0 | 1.0 | 0.0 |
| Antimony trioxide | 10.0 | 10.0 | 0.0 | 10.0 | 10.0 |
| Carnauba wax | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |
| Epoxyasilane *12 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |

Table 2 (cont'd)

| | Example | | | Comparative Example | |
|---------------------------------------|---------|------|------|---------------------|-------|
| | 4 | 5 | 6 | 2 | 3 |
| Gel time (second at 180 °C) | 22 | 25 | 28 | 51 | 21 |
| Fluidity, spiral flow (cm) | 50 | 62 | 87 | 30 | 52 |
| Curing properties | | | | | |
| Moisture absorption (%) *13 | 0.18 | 0.19 | 0.17 | 0.24 | 0.18 |
| Glass transition temperature (°C) *14 | 178 | 171 | 153 | 155 | 176 |
| Solder crack resistance *15 | 0/16 | 0/16 | 0/16 | 16/16 | 14/16 |

(Notes)

*1: F; Ortho-cresol novolak type epoxy resin (trade name of Yuka Shell Epoxy K.K., Epikote 180S65, epoxy equivalent: 214, softening point 67 °C)

*2: G; Tetramethylbiphenol type epoxy resin (trade name of Yuka Shell Epoxy K.K., Epikote XY4000H, epoxy equivalent: 193, melting point 107 °C)

*3: H; Brominated bisphenol A type epoxy resin (trade name of Yuka Shell Epoxy K.K., Epikote 5050, epoxy equivalent: 385, softening point 63 °C, bromine content: 49%)

*4: Melt viscosity of total epoxy resin component mixture, 150 °C, PS

*5: I; Phenol novolak resin (a product of Gun-Ei Kagaku K.K., hydroxyl group equivalent: 105, softening point: 85 °C)

*6: J; Phenol aralkyl resin (trade name of Mitsui Chemical Inc., Milex XL225-3L, hydroxyl group equivalent: 170, softening point: 71 °C)

*7: Mole number of phenolic hydroxyl groups in phenol compound to one mole of total epoxy groups in total epoxy resin component

- *8: K; Methyl (4-methoxyphenyl) (1-naphthylmethyl)sulfoniumhexafluoroantimonate
- *9: L; Methyl (4-hydroxyphenyl)benzylsulfonium hexafluoroantimonate
- 5 *10: M; Triphenyl (4-chlorobenzyl)phosphonium hexafluoroantimonate
- *11: Spherical fused silica powder (trade name of Nippon Aerosil K.K., ELSIL BF100)
- *12: Epoxysilane (trade name of Shin-Etsu Chemical Industry Co., KBM-403)
- 10 *13: Moisture absorption at 85 °C and 85%RH after 168 hours
- *14: Obtained by TMA from transition point on the thermal expansion curve
- 15 *15: 16 specimens (160 pin QFP) were subjected to moisture absorption at 85 °C and 85%RH for 168 hours, and then dipped in a solder bath at 260 °C for 30 seconds. The number of cracked specimens was counted.
- 20 It will be appreciated that the epoxy resin composition of the present invention is excellent in rapid curability and fluidity, and gives a cured product having excellent low moisture absorption, adhesiveness and the like, and therefore can advantageously be used in the field of semiconductor encapsulation or the like.
- 25 Further, the resin encapsulation type semiconductor device of the present invention has excellent solder crack resistance, and therefore can advantageously be used in surface mounting method.

C L A I M S

1. An epoxy resin composition comprising a blend of:
 - (a) an epoxy resin;
 - (b) a compound having two or more phenolic hydroxyl groups on the average in one molecule; and
 - 5 (c) a cationic polymerization catalyst for epoxy resin.
2. The epoxy resin composition as claimed in claim 1, wherein said epoxy resin (a) is an epoxy resin that can be handled as a solid at room temperature, and has a melt viscosity at 150 °C of 2.0 poise or less.
- 10 3. The epoxy resin composition as claimed in claim 1 or 2, wherein said epoxy resin is an amorphous epoxy resin having a softening point of 50 °C or higher.
- 15 4. The epoxy resin composition as claimed in claim 1 or 2, wherein said epoxy resin is a crystalline epoxy resin having a melting point of 40 °C or higher.
- 20 5. The epoxy resin composition as claimed in any one of claims 1 to 4, wherein said compound (b) having two or more phenolic hydroxyl groups on the average in one molecule is blended in an amount so that the phenolic hydroxyl group is 0.05-0.8 mole per mole of epoxy group in the epoxy resin.
- 25 6. The epoxy resin composition as claimed in any one of claims 1 to 5, wherein the cationic polymerization catalyst (c) is at least one catalyst selected from ammonium salts, sulfonium salts, phosphonium salts, and pyridium salts of hexafluorophosphoric acid or hexafluoroantimonic acid.
- 30 7. The epoxy resin composition as claimed in any one of claims 1 to 6, wherein the amount of said cationic polymerization catalyst is 0.01-15 parts by weight per

100 parts by weight of the epoxy resin as the component (a).

8. The epoxy resin composition as claimed in any one of claims 1 to 7, wherein, in addition to components (a), (b) and (c), fused and/or crystalline silica powder fillers are blended as an inorganic filler (d) in an amount of 40-95% by weight based on the weight of the entire composition.

9. A resin encapsulation type semiconductor device, wherein a semiconductor element is encapsulated with a cured product of the epoxy resin composition as claimed in any one of claims 1 to 8.

INTERNATIONAL SEARCH REPORT

Intern. Appl. Application No.

PCT/EP 00/09187

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08K5/13 C08G59/62 C08G59/42 C08K5/00 C08G59/68
 //(C08K5/00, 5:19, 5:375, 5:50)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08K C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|--|-----------------------|
| X | EP 0 235 990 A (DOW CHEMICAL CO) 9 September 1987 (1987-09-09) examples | 1,5,7 |
| A | US 5 610 443 A (INAGAKI AKIHIRO ET AL) 11 March 1997 (1997-03-11) cited in the application column 3, line 55 - column 4, line 21; claims 1,4 | 1,2,6,9 |
| A | EP 0 611 796 A (CIBA GEIGY AG) 24 August 1994 (1994-08-24) page 4, line 9 - line 30; example 1 | 1,6 |
| A | GB 2 055 843 A (CIBA GEIGY AG) 11 March 1981 (1981-03-11) page 2, line 20 - line 33 | 1,5 |

-/-

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
 "E" earlier document but published on or after the international filing date
 "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
 "O" document referring to an oral disclosure, use, exhibition or other means
 "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
 "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
 "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
 "G" document member of the same patent family

Date of the actual completion of the international search

7 February 2001

Date of mailing of the international search report

26/02/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
 NL - 2280 HV Rijswijk
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
 Fax: (+31-70) 340-3016

Authorized officer

Engel, S

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/EP 00/09187

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|---|-----------------------|
| X | DATABASE WPI Section Ch, Week 198409 Derwent Publications Ltd., London, GB; Class A21, AN 1984-051526 XP002159684 & JP 59 008767 A (MITSUI PETROCHEM IND CO LTD), 18 January 1984 (1984-01-18) abstract | 1,5 |
| X,P | DATABASE WPI Section Ch, Week 200067 Derwent Publications Ltd., London, GB; Class A21, AN 2000-681705 XP002159569 & JP 2000 212395 A (SUMITOMO BAKELITE CO LTD), 2 August 2000 (2000-08-02) abstract | 1,5,7,9 |

INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern. Application No.

PCT/EP 00/09187

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---------------------|----------------------------|---------------------|
| EP 0235990 A | 09-09-1987 | AT 68508 T | 15-11-1991 |
| | | AU 584275 B | 18-05-1989 |
| | | AU 6872987 A | 03-09-1987 |
| | | BR 8705759 A | 09-02-1988 |
| | | CA 1277087 A | 27-11-1990 |
| | | DE 3773700 A | 21-11-1991 |
| | | DK 74487 A | 15-08-1987 |
| | | FI 870600 A | 15-08-1987 |
| | | JP 62246919 A | 28-10-1987 |
| | | KR 9303161 B | 23-04-1993 |
| | | NO 870583 A,B, | 17-08-1987 |
| | | PT 84285 A,B | 01-03-1987 |
| | | US 4722981 A | 02-02-1988 |
| | | WO 8705036 A | 27-08-1987 |
| | | ZA 8701070 A | 26-10-1988 |
| US 5610443 A | 11-03-1997 | JP 2875479 B | 31-03-1999 |
| | | JP 8213417 A | 20-08-1996 |
| EP 0611796 A | 24-08-1994 | JP 6271746 A | 27-09-1994 |
| GB 2055843 A | 11-03-1981 | DE 3027140 A | 19-02-1981 |
| | | FR 2461736 A | 06-02-1981 |
| | | JP 56053130 A | 12-05-1981 |
| JP 59008767 A | 18-01-1984 | NONE | |
| JP 2000212395 A | 02-08-2000 | NONE | |